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(54) **Process for the preparation of fluorohalogenated ethers starting from fluorooxy compounds and halogenated olefins.**

(57) Improved process for the preparation of fluorohalogenated ethers by reaction of a fluorinated fluorooxy compound with a halogenated olefin, performed in liquid phase, in the presence of an inert solvent, at low temperature, the fluorooxy compound being continuously fed in form of solution in an inert solvent.

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PROCESS FOR THE PREPARATION OF FLUOROHALOGENATED ETHERS STARTING FROM FLUOROOXY COMPOUNDS AND HALOGENATED OLEFINS

The present invention relates to an improved process for obtaining fluorohalogenated ethers.

The fluorohalogenated ethers prepared according to this process are in particular suitable to be halogenated to give the corresponding perfluorovinylethers.

It is known to react the fluorooxy compounds in gaseous phase, at low temperature, with halogenated olefins to obtain the fluorohalogenated ethers of the above mentioned type (see Italian Patent Application 20781 A/85).

It is well known that fluorooxy compounds having a number of carbon atoms more than 1 are very explosive and they are very difficult to deal with.

Italian Patent Application 20781 A/85 describes a process in which the fluorooxy compound is continuously fed in gaseous phase in order to prepare in a continuous way fluorohalogenated ethers.

The disadvantage of this process resides in the fact that the yield for fluorooxy compounds containing more than two carbon atoms are unsatisfactory.

Due to the fact that the latter fluorooxy compounds are very explosive the teaching of the prior art is very poor.

Object of the present invention is to prepare fluorohalogenated ethers in continuous way by using fluorooxy compounds having more than two carbon atoms.

Object of the present invention is an improved process for preparing fluorohalogenated ether having the general formula:

$(R)_nC(F)_m$ -O - CAF - CA'F$_2$ (1)

wherein A and A' are equal or different and are selected from chlorine and bromine, R is a C_{1-20} alkyl radical or a cycloalkyl, aromatic, heterocyclic or polyether radical containing up to 20 carbon atoms, said radicals being partially or wholly halogenated with bromine, chlorine, iodine and/or fluorine, n is an integer having a value of 1 or 2, m is an integer equal to 3-n, it being understood that the value n = 2 comprises the compounds wherein C belongs to a cyclic ring.

The process is based on the reaction between a fluorooxy compound of the general formula: $(R)_nC(F)_m$ -OF with an olefin CAF = CA'F, wherein the symbols R, A, A' n and m have the above-specified meaning, the reaction being carried out in liquid phase, at a temperature of from -150 to 0°C, preferably -40 to -100°C.

The process is characterized in that the fluorooxy compound is continuously fed into the reactor, in form of a solution in an inert solvent, at a concentration lower than 50% by weight, the mentioned solution being obtained continuously by contacting the fluorooxy compound continuously fed in gaseous form, preferably diluted with an inert gas, with the reaction inert solvent.

As inert gaseous diluent of the starting fluorooxy compounds, the same reaction solvent may be used provided that it is in gaseous form in the compositions in which the fluorooxy compound is supplied. The halogenated olefins must always be present in the reaction phase in excess on the fluorooxy compound. The halogenated olefin may be fed all at the beginning into the reactor in liquid form, optionally diluted with an inert solvent which may be the same solvent used for the fluorooxy compound to be dissolved. Alternatively, also the olefin may be continuously fed.

Solvents suitable for the reaction are, in particular, chlorofluorocarbons, perfluorocarbons and perfluoroethers or perfluoropolyethers.

In the process according to the invention, the fluorooxy compound coming directly from the reactor of the synthesis of the same, in gaseous form, can be advantageously used. In fact, the inert diluents used in the reaction for the synthesis of the fluorooxy compound starting from fluorine and acyl fluoride can be compatible and suitable also for the present process.

Examples of perfluorohalogenated ethers which may be prepared by the process according to the invention are as follows:

CF_3-CF_2-O-CClF-$CClF_2$
$CClF_2$-CF_2-O-CClF-$CClF_2$
CCl_2F-CF_2-O-CClF-$CClF_2$
CCl_3-CF_2-O-CClF-$CClF_2$
$CBrF_2$-CF_2-O-CClF-$CClF_2$
CF_3-O-CF_2-CF_2-O-CClF-$CClF_2$
C_2F_5-O-CF_2-CF_2-O-CClF-$CClF_2$
$(CF_2)_2$-CF-O-CClF-$CClF_2$.

The following examples are given only to illustrate the possible performance of the process according to the invention.

EXAMPLE 1

A gaseous stream of fluorooxyperfluoroethane obtained by reacting trifluoroacetylfluoride and elemental fluorine fed separately into a catalytic reactor in the presence of ALGOFLON A114® - (dichlorotetrafluoroethane) in the gaseous phase, contains 20 % by volume of C_2F_5OF and 80 % of $C_2F_4Cl_2$.

This gaseous stream is cooled in a glass con-

denser externally cooled to -80°C with a flow of 18.7 Nl/h and is for the most part condensed. The thus obtained solution is added dropwise into a reactor cooled to -80°C containing a strongly agitated solution of symmetric difluoroethylene (230 g) in 600 g of ALGOFLON A12® (CF_2Cl_2).

After 10 hours the fed perfluorooxy compound is equivalent to 95 % of the olefin. The feeding is interrupted and the liquid in the reactor is distilled off.

A fraction of product boiling at 58 - 60°C (356 g; yield 80%) is recovered and identified as CF_3-CF_2-O-CFCl-CF_2Cl by the mass spectrometry.

EXAMPLE 2

A gaseous stream containing 20 % by volume of chlorotetrafluorooxyethane CF_2Cl-CF_2-OF and 80 % by volume of ALGOFLON A114® obtained as in the preceding example is cooled in a condenser cooled to -30°C wherein it condenses almost completely and the thus obtained solution is added dropwise into a strongly agitated reactor, externally cooled to -80°C and containing 200 g of olefin CFCl=CFCl dissolved in 500 g of ALGOFLON A114®.

After 20 hours, always keeping the flow of the gas at 7.8 Nl/h the fed fluorooxy compound is about 92 % of the olefin. At this moment the feeding is interrupted, the content of the reactor is distilled off and 79 g of a fraction boiling at 90 - 95°C, is recovered,the 95 % of which consists of the compound CF_2Cl-CF_2-O-CFCl-CF_2Cl identified by mass spectrometry.

Claims

1. A process for the preparation of fluorohalogenated ethers having the general formula:

$$(R)_nC(F)_m\text{-}O\text{-}CAF\text{-}CA'F_2$$

wherein A and A' are equal or different and are selected from chlorine or bromine, R is a $C_{1\text{-}20}$ alkyl radical or a cycloalkyl, aromatic, heterocyclic or polyether radical containing up to 20 carbon atoms, said radicals being partially or wholly halogenated with bromine, chlorine, iodine and/or fluorine, n is an integer chosen from 1 or 2, m is an integer equal to 3-n, wherein the value n=2 comprises the compounds wherein C belongs to a cyclic ring, which process comprises reacting in liquid phase a fluorooxy compound $(R)_n$ $C(F)_m$-OF with an olefin CAF=CA'F, at a temperature of from -150 to 0°C, characterized in that the fluorooxy compound is continuously fed in the reaction phase, in form of a solution with a concentration lower than 50% by weight in an inert solvent, the olefin being fed in the liquid state, optionally in an inert solvent, all at the beginning into the reactor or continuously, in such a manner to have always an excess of the olefin in the reaction phase.

2. The process according to claim 1, wherein a chlorofluorocarbon or a perfluorocarbon or a perfluoroether or a perfluoropolyether is used as inert solvent.

3. The process according to claim 1 or 2, wherein the reaction is carried out at a temperature of from -40°C to -100°C.

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EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 87116811.8

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,X	EP - A1 - 0 201 871 (AUSIMONT) * Claims 1,15 *	1	C 07 C 43/12 C 07 C 41/06
D,X	& IT-A-2 078 185 --		
X	GB - A - 2 148 286 (OCCIDENTAL CHEMICAL) * Claims 1,3-7 * ----	1-3	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 07 C 43/00
C 07 c 41/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	15-02-1988	REIF

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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